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To: Dr. D. Mills
Director of Research

MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS DURING THE 1990 EULERIAN MODEL EVALUATION FIELD STUDY

T. Jarv and C. Brain
Environmental Science Section
Chemical Research Department

ABSTRACT

An improved technique for measuring ambient concentrations of volatile organic compounds has been developed. The technique was used to analyze air samples obtained during the second field campaign of the Eulerian Model Evaluation Field Study, March 16 to April 29, 1990. This report describes the analysis method and lists the observed concentrations measured in air samples collected during the study.

1.0 INTRODUCTION

Elevated ozone episodes are a recurring phenomenon during Ontario summers. To advance our understanding of the role of nitrogen oxides (NO_x) vs volatile organic compounds (VOCs) and biogenic vs anthropogenic emissions in controlling ozone and other oxidant concentrations in Ontario, an intensive field study (the Canadian component of the Eulerian Model Evaluation Field Study - EMEFS) was undertaken during the summer of 1988 by the Atmospheric Environment Service of Canada (Dr. K. Puckett, Coordinator), with support from a number of collaborators, including Ontario Hydro. A second intensive field campaign of EMEFS was undertaken during the spring of 1990 to investigate the effect of season on the production of biogenic VOCs and the formation of ozone and other oxidants. The latest study included the measurement of VOCs at two sites, Egbert and Lake Traverse, in rural south-central Ontario over a period of 55 days from March 16 to April 29, 1990.

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This report describes improvements in the analysis technique that has been developed to measure VOCs in ambient air. The work in this report was carried out to support the development of an information base on biogenic and anthropogenic VOCs. Under the auspices of the Canadian Institute for Research in Atmospheric Chemistry (CIRAC), this data set will be used to examine the observed mixing ratios of different classes of VOCs, to determine the relative contribution of natural and anthropogenic sources towards the local oxidant abundance, and to test the predictive capability of the Canadian and US Eulerian long-range transport models (ADOM and RADM). Ontario Hydro will use the data set to investigate the role of its NO_x emissions in ozone formation in Ontario under a variety of emission scenarios.

2.0 SAMPLING

2.1 Location

Samples were collected during March 16 to April 29, 1990 at two ground sites in Ontario - Egbert and Lake Traverse. The two sites are about 240 km apart and located roughly along the prevailing air mass trajectory associated with high ozone concentrations. For a period of 55 days air samples were collected three times a day (at approximately 8 AM, 4 PM and 10 PM). During the same period, samples were also collected from a research aircraft (a Twin Otter) whenever it was close to the fixed ground sites and during intensive sampling days.

2.2 Participating Laboratories

Analysis of the air samples was performed by Concord Environmental (for C2-C6), York University, Ontario Hydro, Ontario Ministry of the Environment and Environment Canada. This report presents Ontario Hydro's results only.

3.0 EXPERIMENTAL

3.1 Sampling

Air samples were collected in SUMMA stainless steel canisters. The interior surfaces of these canisters had been electropolished using the Molectrics SUMMA process. This process has been shown to result in canisters with an excellent stability for hydrocarbons and halocarbons/2/.

The canisters were cleaned between samples at York University by flushing with humidified ultra clean air, heating to 80°C and then evacuating to 10^{-6} Torr.

An ultra-clean air pump (Model FC-1121, 12V DC Motor, Biosphere Research Corporation) was used to fill the canisters with ambient air. This pump has a Teflon diaphragm and stainless steel plate

pump head, and a flow capacity of 6 L/min. Each canister was pressured to about 35 psig, providing about 6 L of sample, at ambient pressure.

3.2 Analytical System

The gas chromatographic (gc) analytical system used in the 1988 VOCs study/1/ was modified. A dual capillary column gc system/3/ and a commercial concentrator/desorber system (Tekmar 5010GT) were mated to perform the analysis described in this report. The modified Tekmar 5010GT and the gc analytical system are shown in Figures 1 and 2, respectively. An air sample volume of about 0.2 L is necessary to achieve the desired lower limits of detection (0.1 - 0.02 $\mu g/m^3$) for the various hydrocarbons and halocarbons in the atmosphere. Therefore, sample preconcentration is necessary to reduce the sample size sufficiently to allow injection and subsequent separation with the gc system.

The modified Tekmar Model 5010GT Automatic Desorber shown in Figure 1 was used to preconcentrate the air sample. All pathways are inert, either glass-lined stainless steel or fused silica tubing. Once the internal cryogenic trap is loaded, it is heated, transferring all VOC analytes onto a cryogenically cooled capillary interface. The capillary interface focuses the analytes at the head of the capillary columns. After all the analytes are transferred, the capillary interface is heated, sending a tight slug of analytes onto the capillary columns in the gc.

3.3 Experimental Procedure

To analyze the air contained in the pressurized SUMMA-treated stainless steel canisters, the Tekmar Model 5010GT was modified to load the canister aliquot directly onto the internal cryogenic trap. Figure 1 shows the original Tekmar 5010GT configuration, with all valves and system changes marked. A 1/8" nickel line was connected from the sample inlet port at the rear of the Tekmar unit to the canister. The tee at the base of the furnace ('A' in Figure 1) was capped on the furnace side. The sample inlet line was rerouted to the normally closed (NC) side of V1 and the normally open (NO) end was capped. This allowed the air sample from the canister to enter V4 through port 5 of the 8-port valve and exit through port 4 to be concentrated on the internal cryogenic trap directly, bypassing the furnace. The air continues through the trap, through ports 6 and 7, and out the trap vent.

With the above modifications, the air sample was loaded onto the cryotrap with the Tekmar in the desorb mode. At this time, the vent valve V1 opened, allowing the contents of the pressurized canister to flow. A Tylan Corporation mass flow controller (100 mL/min) along with an ADI diaphragm pump attached to the trap vent

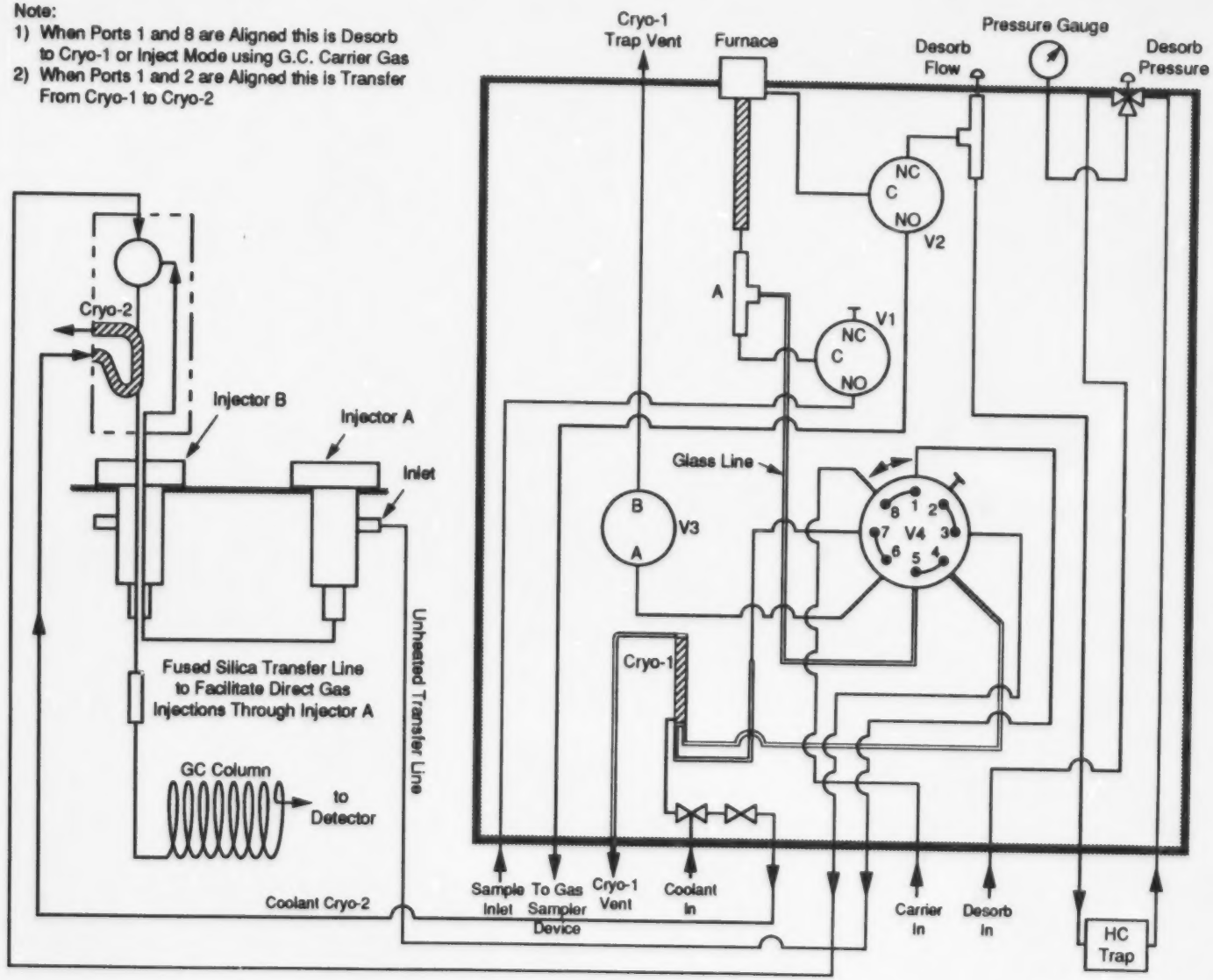

Figure 1

Schematic Diagram of Tekmar 5010 GT Concentrator/Desorber System

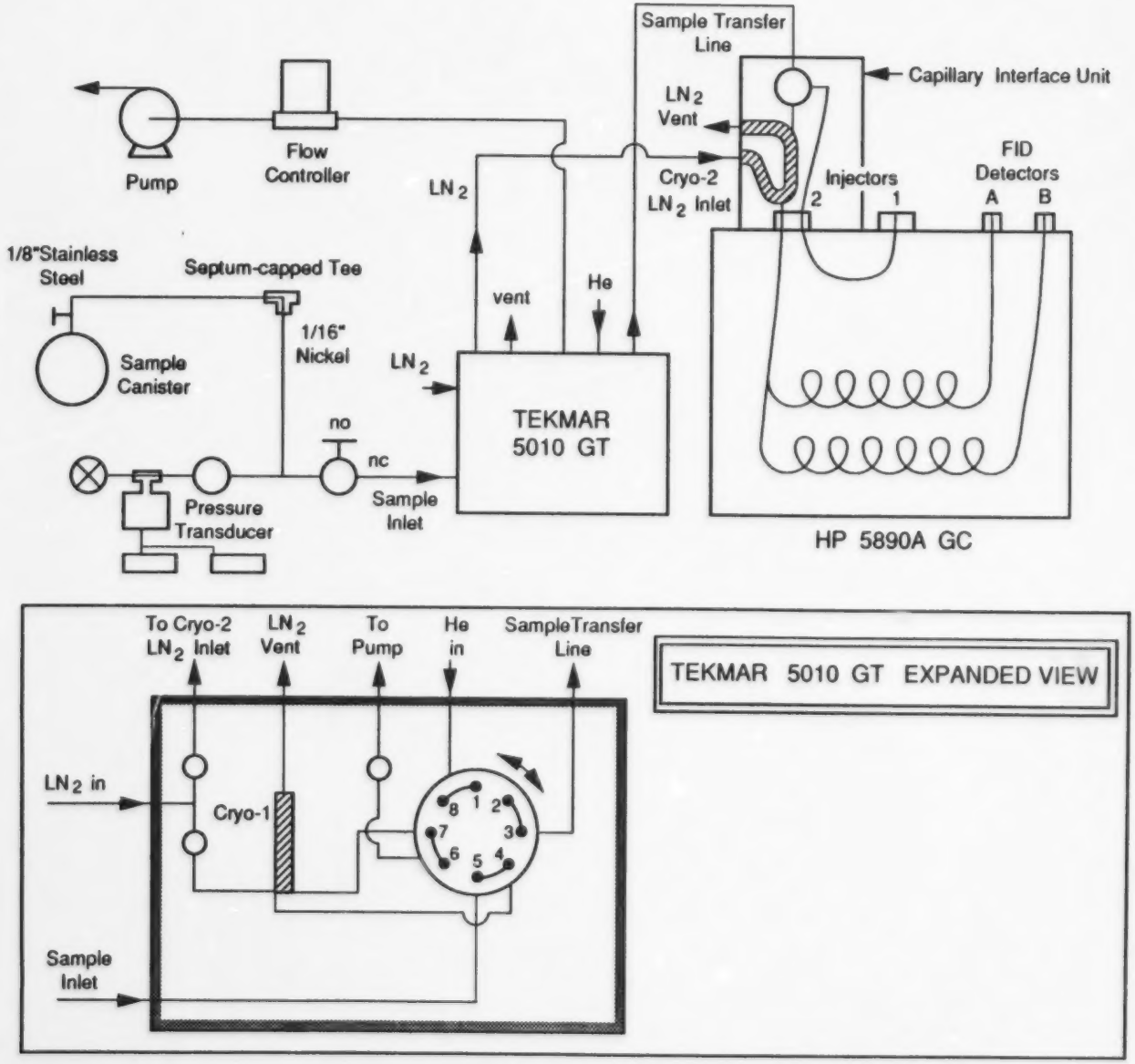
Sample Transfer Line
Capillary Interface Unit
LN2 Vent
Flow Controller
Pump
LN2
Cryo-2 LN2 Inlet
Injectors
FID Detectors
2
1
A
B
1/8"Stainless Steel
Septum-capped Tee
1/16" Nickel
Sample Canister
vent
He
LN2
TEKMAR 5010 GT
no
nc
Pressure Transducer
Sample Inlet
HP 5890A GC
To Cryo-2 LN2 Inlet
LN2 Vent
To Pump
He in
SampleTransfer Line
TEKMAR 5010 GT EXPANDED VIEW
LN2 in
Cryo-1
8
1
2
3
4
5
6
7
Sample Inlet

Figure 2

regulated the flow from the canister. The volume of sample concentrated onto the trap was determined from the desorb time and the mass flow controller flowrate.

An injection tee, with one leg sealed with a septum, was placed in the nickel line downstream of the canister to allow a gas standard and/or a primary internal standard (hexane) to be injected directly onto the Tekmar internal cryotrap.

Once the analytes are trapped on the Tekmar internal cryotrap, the capillary interface cryotrap, located on the HP 5890A gc, is cooled to -150°C. The Tekmar internal cryotrap is then heated to 80°C, as helium carrier is passed through, to sweep the desorbed analytes from the trap through the heated fused silica sample transfer line (150°C) to the capillary interface cryotrap. As the Tekmar is operating, the oven of the HP-5890A gc is cooled to -60°C in preparation for sample analysis. Sample injection from the capillary interface cryotrap occurs by rapidly raising the temperature to 150°C to release a tight slug of analytes onto the head of the two capillary columns.

Water vapour that is collected in the internal cryotrap is carried over to the cooled capillary interface cryotrap during the sample transfer step, thus leading to column plugging and disruption of flow through the analytical columns. To minimize transfer problems, the air sample volume concentrated onto the Tekmar internal cryotrap was limited to about 120 mL.

3.4 Separation

In the cold gc oven (-60°C), the tight slug of analytes is assumed to be distributed about equally and in a reproducible fashion through the Chromfit 'Y' connector that interfaces the two capillary columns (DB-1 and DB-5, 30 m x 0.32 mm ID, J&W Scientific) to the uncoated fused silica retention gap coming from the capillary interface cryotrap.

The gc oven temperature is kept at -60°C for the first 2 minutes of the analysis. The oven temperature is then increased at a ramp rate of 6°C/min to reach a final temperature of 210°C. Compounds eluting from each column were detected with flame ionization detectors (FID) operating at 250°C. The signal from each detector was recorded, integrated, analyzed and saved as data files by the HP-3365 ChemStation software running on a Tandy 4000SX microcomputer.

3.5 Calibration

The VOCs on the target list were either gases or liquids. Therefore, two different types of standard methods were used for the calibrations. The gaseous standards were obtained from Supelco and Scott Specialty Gases as traceable primary gas mixtures. The

apparatus was calibrated by injecting standard gas mixtures at the septum-capped tee and flushing the components onto the Tekmar internal cold trap. Each analysis contained a hexane reference injection (20.5 ppm, 250 µL) as an internal standard. Linear regression analysis using at least three different concentrations per compound was used to obtain the signal response relationship for each target VOC.

Standard liquids, available as "Theta Kits", were obtained from Ultra Scientific, Rhode Island, USA and Accustandard, Connecticut, USA, as pure, or in some cases as certified diluted concentrations. Multi-component mixtures were prepared using a static dilution bottle technique (US-EPA method B011586). At least three concentrations were used for each target VOC to generate a calibrated response curve.

For all gaseous and liquid standards, the FID response for each target VOC was calibrated relative to the full amount injected since the exact sample split ratio between the two capillary columns could not be precisely determined.

The gc performance was checked with each analysis using a primary standard (±1%) of hexane (20.5 ppm) as an internal standard.

4.0 ACCURACY AND PRECISION OF THE METHOD

The analytical procedure consists of three main operations:

(1) Measurement of the volume of air sample to be concentrated;

(2) Trapping and subsequent release of the hydrocarbons to be determined; and

(3) Gas-chromatographic analysis of the individual hydrocarbons.

4.1 Measurement of Air Sample Volume

The air sample volume was determined by controlling the pumping rate of air extracted from the canister for a predetermined sampling time. A Tylan Corporation Model FC-280 (100 mL/min) mass flow controller and RO-20A control box, set at 20 mL/min, in conjunction with an ADS Model 01310T diaphragm pump was used to control the flow rate through the Tekmar internal cryogenic trap. The sampling time was controlled by the desorb instruction of Method 1 resident in the Tekmar unit. Typical sampling times were between 5 and 8 minutes.

4.2 Trapping and Release of Hydrocarbons

The VOC recovery of the canister preconcentration procedure was measured with replicate injections of 250 µL of a standard gas mixture containing about 15 ppm each of C3 to C6 straight chain hydrocarbons. Injections were made into the preconcentration trap at -150°C and also directly into the capillary interface trap on the gc, in which case the recovery was assumed to be 100%. The mean recovery from the preconcentration loop was found to be >85% for C5 and C6 compounds. C3 and C4 recovery was variable due to the difficulty of retaining the more volatile hydrocarbons on the Tekmar internal 1/16" glass-lined steel trap.

4.3 Precision of the Analytical Procedure

The precision of the preconcentration method was determined from replicate analyses of a primary standard of hexane (20.5 ppm, Matheson) using repeat syringe injections of different volumes. The syringe injection and Tekmar Method 1 precision was determined to be better than 5.8%.

4.4 Limits of Detection and Concentration Range

The limits of detection depend on the individual hydrocarbon species and on the volume concentrated. For a typical 120 mL air sample, the practical detection limits of the VOCs ranged from about 0.11 to 26.5 $\mu g/m^3$ (see Appendix 4).

4.5 Hydrocarbon Species Identification

The analysis of air samples for VOCs by preconcentration fcllowed by gas chromatography with selective detection (FID) was adequate for the initial EMEFS study as long as the compounds of interest were known. To extend the confidence in the gas chromatographic analysis by FID, a dual column procedure, originally developed for PCB analysis/3/, was established. Another choice would have been to use gas chromatography/mass spectrometry for the screening, however, this option was unavailable. The results from the first EMEFS study were used as a basis for predetermining the major species likely to be encountered in the atmospheric samples.

The FID signals from each chromatographic column were integrated separately by HP 3365 ChemStation software and stored as sample files. The files were then transferred to a Digital MicroVAX computer for final analysis and reporting. A cross comparison of identified compounds and concentrations for each capillary column was made by the MicroVAX software. VOCs that were identified on both columns are reported and an average concentration calculated for each species.

5.0 RESULTS

The results for the samples analyzed by Ontario Hydro are listed in Appendices 1 to 3. Appendix 1 lists the results for the samples taken at Lake Traverse, Appendix 2 lists the results for the samples taken at Egbert and Appendix 3 lists the results for the samples taken from the aircraft. Preceding Appendix 1 is a description of the sampling notation, ie, site, sample date, time, etc.

A detailed analysis of the results of this study is beyond the scope of this report. These data will be part of a larger data base that will receive further study under the auspices of the Canadian Institute for Research in Atmospheric Chemistry (CIRAC). Ontario Hydro will make use of this data set in its studies of the role of power plant NO_x emissions in ozone formation in Ontario.

6.0 CONCLUSIONS

1. A modified technique has been developed for the cryogenic concentration of ambient air sample and subsequent dual-capillary-column gas chromatographic analysis of condensible hydrocarbons.

2. The technique has been shown to be suitable for the concentration of hydrocarbons in the carbon range C4 to C10.

7.0 SUGGESTED IMPROVEMENTS

1. The sample volume throughput of the cryogenic preconcentration step is limited by the moisture that is trapped and then transferred during the desorption step, to the capillary interface cryogenic trap at the head of the gas chromatographic columns. Methods to reduce the water that is trapped and subsequently carried over must be investigated to improve the analytical sensitivity towards the VOCs.

2. A more expensive solution for reliable VOC identification is to establish a gas chromatography/mass spectrometry system to analyze the air samples.

3. The integrity of the samples stored in canisters prior to analysis remains to be thoroughly investigated. Aging of the field samples, effectiveness of the canister cleanup and effect of storage conditions (ie, temperature) need to be investigated to establish the reliability of the field sampling method.

Approved by:

D.J.R. Dodd
Manager
Chemical Research Department

Prepared by:

T. Jarv
Scientist
Environmental Science Section

Reviewed by:

O.T. Melo
Supervising Engineer
Environmental Science Section

C. Brain
Technician
Environmental Science Section

REFERENCES

1. Handy, B., (1989), "Measurement of Biogenic and Anthropogenic Volatile Organic Compounds During the Canadian Atmospheric Chemistry Study, July 17 to August 31, 1988," Ontario Hydro Research Division Report No 89-262-K.

2. Rudolph, J., F.J. Johnen and A. Khedim, (1986), "Problems Connected with the Analysis of Hydrocarbons and Halocarbons in the Non-Urban Atmosphere." International Journal of Environmental Analytical Chemistry, 27, 97-122.

3. Jayanty, R.K.M. (1989). "Evaluation of Sampling and Analytical Methods for Monitoring Toxic Organics in Air." Atmospheric Environment 23, 777-782.